

# Hydrocarbons in the Non-Urban Atmosphere: Analysis, Ambient Concentrations and Impact on the Chemistry of the Atmosphere<sup>†</sup>

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The role of hydrocarbons for the chemistry of the atmosphere outside of heavily polluted urban or industrial areas is not yet fully understood. One of the reasons is the rather limited data base for hydrocarbon mixing ratios in rural and semi-rural areas. This is—at least partly—due to analytical problems. The mixing ratios of hydrocarbons—except methane—in remote and semi-remote areas are very low, a few ppb or even less. In addition, the hydrocarbon pattern is—especially in semi-rural areas—extremely complex, a potpourri of engine exhaust, refinery emissions, natural gas leakage, biogenic emissions from plants, decaying leaves etc.

In the past few years we have developed gas chromatographic techniques for the identification and quantification of low and medium molecular weight hydrocarbons outside polluted areas. The results of these measurements show that these non-methane hydrocarbons (NMHC) are present in the non-urban atmosphere at very low mixing ratios—generally fractions of a ppb, rarely more than 1 ppb. Nevertheless, many of these hydrocarbons are very reactive (rather high rate constants for reaction with OH, some of these hydrocarbons—the alkenes—also react with ozone) and thus are of considerable importance for the chemistry of the atmosphere.

In this paper we present atmospheric measurements of some non-methane hydrocarbons in different remote, rural and semi-rural areas. These measurements allow some inferences on the impact of man made hydrocarbons on the chemistry of the atmosphere outside urban and industrialized areas.

**KEY WORDS:** Hydrocarbons, atmosphere, rural areas, background, measurements

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## INTRODUCTION

The important role of non-methane hydrocarbons for the photochemical reaction cycles in urban and industrialized areas has long been recognized. As far as non-urban areas are concerned methane is often the only hydrocarbon compound which is considered as important for the chemistry of the atmosphere. However, since a couple of years it is known that non-methane hydrocarbons can be quite important for the various chemical reactions which are taking place in the remote troposphere. This fact seems to be rather surprising if we have a look at the mixing ratios of some of the different hydrocarbons which can be found in rural continental areas. Table I presents the mixing ratios of a number of hydrocarbons measured at a remote rural site in continental Germany. If we compare the mixing ratio of CH<sub>4</sub> with that of the other hydrocarbons, we see that methane is roughly three orders of magnitude more abundant than each of the other hydrocarbons. This indeed suggests that methane might be the only hydrocarbon compound which is important for the chemistry of the atmosphere. At a closer inspection this conclusion however seems premature. The atmospheric reaction chain of hydrocarbon oxidation starts mainly with the attack of an OH radical:



The conversion rate for a given hydrocarbon in the atmosphere then can be written as:

$$r_{\text{OH}} = k_{\text{OH}}[\text{RH}][\text{OH}]$$

From this it is evident that for a comparison of the different hydrocarbons with respect to their participation in atmospheric chemistry we have to consider the reaction rate constants as well as the atmospheric concentrations of the individual hydrocarbons if we want to compare their atmospheric reaction rate. Therefore we included in Table I the product of reaction rate constant and atmospheric mixing ratio to allow a direct comparison of the different hydrocarbons. We can see that the turnover rates for the

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TABLE I

Mixing ratios and conversion rates for selected hydrocarbons measured at an atmospheric background station (Deuselbach, Hunsrück) in Germany on 23 October 1983, 14:30 h.

| Compound  | Mixing ratio (ppb) | $k_{\text{OH}}^a$ (cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ) | MR · $k_{\text{OH}}$ · 10 <sup>11</sup> [cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ] | MR $k_{\text{OH}}$ / MR <sub>CH<sub>4</sub></sub> · $k_{\text{OH}}^{\text{CH}_4}$ (%) |
|---|--------------------|--|--|---|
| [CH <sub>4</sub>  | 1740               | 8.0 · 10 <sup>-13</sup>  | 1.4  | 100   |
| C <sub>2</sub> H <sub>6</sub>                               | 1.55               | 2.9 · 10 <sup>-12</sup>  | 4.5 · 10 <sup>-2</sup>   | 6.4   |
| C <sub>2</sub> H <sub>4</sub>                               | 0.72               | 1.5 · 10 <sup>-12</sup>  | 0.11   | 24  |
| <i>n</i> -C <sub>3</sub> H <sub>10</sub>                    | 0.54               | 2.5 · 10 <sup>-12</sup>  | 0.14   | 40  |
| <i>n</i> -C <sub>3</sub> H <sub>12</sub>                    | 0.14               | 3.7 · 10 <sup>-12</sup>  | 5.2 · 10 <sup>-2</sup>   | 19  |
| <i>n</i> -C <sub>3</sub> H <sub>14</sub>                    | 0.051              | 4.8 · 10 <sup>-12</sup>  | 2.4 · 10 <sup>-2</sup>   | 10  |
| <i>n</i> -C <sub>3</sub> H <sub>16</sub>                    | 0.044              | 5.9 · 10 <sup>-12</sup>  | 2.6 · 10 <sup>-2</sup>   | 13  |
| <i>n</i> -C <sub>3</sub> H <sub>18</sub>                    | 0.014              | 7.0 · 10 <sup>-12</sup>  | 1.0 · 10 <sup>-2</sup>   | 6   |
| <i>n</i> -C <sub>3</sub> H <sub>20</sub>                    | <0.01              | <8.1 · 10 <sup>-12</sup>   | <8.0 · 10 <sup>-2</sup>  | <5  |
| <i>n</i> -C <sub>3</sub> H <sub>22</sub>                    | <0.01              | <9.2 · 10 <sup>-12</sup>   | <9.0 · 10 <sup>-2</sup>  | <6  |
| <i>i</i> -C <sub>3</sub> H <sub>10</sub>                    | 0.22               | 2.4 · 10 <sup>-12</sup>  | 5.3 · 10 <sup>-2</sup>   | 15  |
| <i>i</i> -C <sub>3</sub> H <sub>12</sub>                    | 0.25               | 4.6 · 10 <sup>-12</sup>  | 0.12   | 43  |
| C <sub>2</sub> H <sub>2</sub>                               | 0.60               | 8.1 · 10 <sup>-11</sup>  | 0.49   | 70  |
| C <sub>2</sub> H <sub>2</sub>                               | 0.10               | 1.5 · 10 <sup>-11</sup>  | 0.15   | 32  |
| C <sub>2</sub> H <sub>2</sub>                               | 0.59               | 1.6 · 10 <sup>-12</sup>  | 9.4 · 10 <sup>-3</sup>   | 1   |
| C <sub>2</sub> H <sub>6</sub>                               | 0.12               | 1.2 · 10 <sup>-12</sup>  | 1.4 · 10 <sup>-2</sup>   | 6   |
| C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub>               | 0.18               | 6.4 · 10 <sup>-12</sup>  | 0.12   | 43  |
| <i>p</i> -Xylol   | 0.04               | 1.5 · 10 <sup>-11</sup>  | 0.06-0.1   | 34-57   |
| <i>m</i> -Xylol   | 0.02               | 2.4 · 10 <sup>-11</sup>  | 3.0 · 10 <sup>-2</sup>   | 17  |
| <i>o</i> -Xylol   | 0.02               | 1.4 · 10 <sup>-11</sup>  | 3.0 · 10 <sup>-2</sup>   | 17  |
| C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> | 0.05               | 7.5 · 10 <sup>-12</sup>  | 3.8 · 10 <sup>-2</sup>   | 22  |

Deuselbach 23.10.83, 14:30h  
CO 213ppb

<sup>a</sup>The reaction rate constants are taken from Ref. 3

various hydrocarbons are significantly lower than for methane, but in total the NMHC conversion rates exceed that of methane. If we estimate the turnover rates for the different hydrocarbons in terms of carbon atoms instead of molecules (that is we have to multiply the atmospheric conversion rates for each individual hydrocarbon with the number of carbon atoms in this compound) we can see that the NMHC in total exceed methane by far. It should be noted that this

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air sample contained 210 ppb CO, a value which is comparable to CO mixing ratios which were reported by Schmidt *et al.*<sup>1</sup> in the free troposphere over North America.

It is obvious that such simple estimates as above do not give an exact picture of the actual impact of the various NHMCs on the chemistry of the atmosphere. The intermediate products of the hydrocarbon oxidation chains (e.g. aldehydes, ketones, alkylperoxides, etc.) may be removed from the atmosphere by wet or dry deposition. On the other side most of the intermediate products of NHMC oxidation are considerably more complex than the products of methane oxidation and thus can open new pathways in the chemistry of the atmosphere (e.g. Duce *et al.*<sup>2</sup>). From these considerations it is evident that for a thorough understanding of the chemistry of the atmosphere in remote or semi-remote areas we need information on the mixing ratios of the various non-methane hydrocarbons. Unfortunately the existing data base is far from being complete.

There are a few measurements of light hydrocarbons in the remote marine atmosphere, data from the interfacial region between urban polluted areas and the remote unpolluted atmosphere are nearly completely missing.<sup>3</sup> In the past few years we made a number of measurements of light and medium molecular weight hydrocarbons in the atmosphere outside polluted areas. In this paper we will present some results from measurements in remote and semi-remote areas.

#### MEASUREMENT TECHNIQUES

The air samples are collected in evacuated, carefully pretreated stainless steel containers with metal bellow valves. The samples are afterwards analyzed in the laboratory by different gas chromatographic techniques. The hydrocarbons are preconcentrated from typically 0.5–2 dm<sup>3</sup> of air (STP) on solid sorbents (porous glass beads, porous silica, carbosieve) at subambient temperatures. The light hydrocarbons (C<sub>2</sub>–C<sub>3</sub>) are separated on packed stainless steel columns (inner diameter 0.8 mm, length 5–10 m). As column packings porous silica, modified porous silica (Porasil C-*n*-octane) or porous polymers (Parapak Q or QS) are used. The choice of the

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stationary-phase depends in each case on the compounds on which our main interest is focussed. The hydrocarbons with more than 5 carbon atoms are separated on glass or quartz capillary columns with stationary phases of low polarity (OV-101, SE-30, DB 1). For hydrocarbon measurements flame ionisation- or photoionisation detectors (10.2 eV) are used. With flame ionisation detection the lower limit of detection ( $3\sigma$ ) is typically 10–20 ppt in a 1 dm<sup>3</sup> (STP) air sample for packed columns and 5–10 ppt with capillary columns. Compounds with high photoionisation cross-sections such as aromatics and most of the alkenes have between a factor of 3 and 20 lower detection limits with a photoionisation detector (10.2 eV lamp) compared to a flame ionisation detector. The precision of the measurements is generally better than 15%, typically between 5% and 10%.

#### HYDROCARBONS IN THE REMOTE AND SEMI-REMOTE CONTINENTAL ATMOSPHERE

If we consider the large number of different hydrocarbons which are emitted from various industrial, urban and natural sources<sup>4</sup> and the rather short atmospheric residence times for most of the hydrocarbons of a few days or even less<sup>4</sup> we can expect a considerable variability with time, location, meteorological conditions etc. Thus it will be extremely difficult to define general "continental background" values for hydrocarbon mixing ratios. Instead of trying to do so we will present some results we obtained from several measurement series at different rural continental locations and look for the factors which may determine or influence the hydrocarbon composition of the atmosphere over remote or semi-remote continental areas.

In Figure 1 the results of some selected measurements are shown to demonstrate the variability of the hydrocarbon mixing ratios in non-urban areas. Two of the measurements were made at a rural site near Jülich but with the wind from different directions. A third sample was collected on a remote mountain station in the Black Forest at 1280 m altitude which was above the boundary layer during sampling. Also included for comparison are the results listed in Table I. The different sampling locations are shown in Figure 2.

At first sight it is rather surprising that the two measurements at

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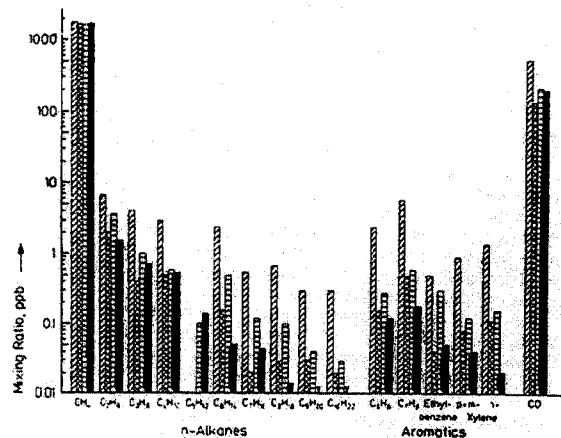


FIGURE 1 Measurements of *n*-alkanes and light aromatics in the non-urban atmosphere:

hatched bars: Spiel, 25 Sept. 1982, easterly wind  
 cross hatched bars: Spiel, 28 Sept. 1982, westerly wind  
 vertically lined bars: Schauinsland, 18 Febr. 1983  
 solid bars: Deuselbach, 23 Oct. 1983

The downward errors indicate that the hydrocarbon mixing ratios are below the detection limit.

Spiel (near Jülich) show such large differences in hydrocarbon mixing ratios—up to an order of magnitude for some compounds. However, a look at the map (Figure 2) explains this. With wind from the east, the sampling location is heavily influenced by air masses from industrialized and densely populated areas which are located only 30–100 km east of Spiel, whereas, there is no major industrialized area for more than 200 km west of Spiel. This shows that transport can strongly influence the hydrocarbon mixing ratios in rural areas

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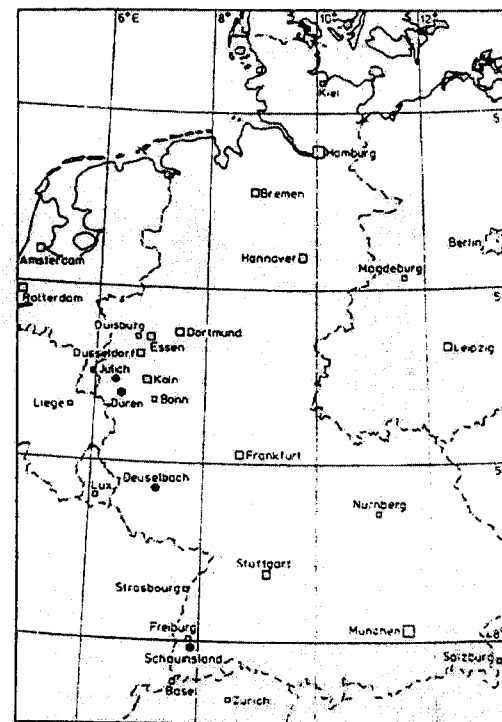


FIGURE 2 Map showing the sampling locations for measurements of hydrocarbons outside areas in West Germany (full circles).

and we may expect extreme variations in the hydrocarbon mixing ratios even outside urban areas.

Nevertheless we observe some features in the hydrocarbon profiles which deserve interest. For the *n*-alkanes the atmospheric mixing ratios show a considerable decrease with increasing carbon number. We also observe that the differences in mixing ratios between the different samples seem to increase with increasing carbon number, e.g. for  $\text{CH}_4$  the variation is only a few percent, for  $\text{C}_2\text{H}_6$  the highest and lowest mixing ratios differ by a factor of about 4 and for  $n\text{-C}_8\text{H}_{18}$  this factor is nearly 50. Similar observations can be made for the light aromatics, the benzene mixing ratios in Figure 1 vary about a factor of 20, the *o*-xylene values more than a factor of 50. This indicates that hydrocarbons of lower reactivity, e.g. ethane, show much less pronounced variations in their atmospheric mixing ratios than highly reactive species such as xylene. Moreover it seems that the air samples with the largest hydrocarbon mixing ratios show the least pronounced difference between the hydrocarbons of different reactivity, e.g. for sample No. 1 with 6.8 ppb of  $\text{C}_2\text{H}_6$  the ratio  $\text{C}_2\text{H}_6/\text{C}_8\text{H}_{18}$  is about 10, for sample No. 4 with only 1.55 ppb of  $\text{C}_2\text{H}_6$  this ratio amounts to about 100. Similar observations can be made for the light aromatic species.

This suggests that dilution as well as photochemical oxidation are important factors which govern the hydrocarbon mixing ratios in remote continental areas. However, it would be premature to draw such conclusions from only 4 measurements.

Thus we will look at the matter in some more detail. Table II shows the results of several measurements which were made in March 1984 in a semi-rural area near Düren (see Figure 2). From the rather high mixing ratios of predominantly man-made species such as the light aromatic hydrocarbons or CO and  $\text{C}_2\text{H}_2$  it is evident that the sampled air is substantially influenced by strong anthropogenic hydrocarbon sources. Indeed the relative pattern of the hydrocarbons is very similar to results reported for some major cities in the U.S.,<sup>5</sup> however the absolute mixing ratios listed in Table II are generally somewhat lower. We can compare these data from areas with significant pollution with measurements from a more remote site in continental Europe. In Table III the results of three series of measurements at a "background station" (Deuselbach) are shown. Each of the series consisted of at least 6 measurements. These

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TABLE II  
Hydrocarbon mixing ratios in a semi-rural area near Düren, average from 5 measurements in March 1984.

| Compound  | Mixing ratio (ppb) |
|---|--------------------|
| $\text{CH}_4$   | 1970 ± 110         |
| $\text{C}_2\text{H}_6$                                      | 5.3 ± 0.7          |
| $\text{C}_2\text{H}_4$                                      | 6.6 ± 3.7          |
| $\text{C}_2\text{H}_2$                                      | 5.8 ± 3.8          |
| $\text{C}_3\text{H}_8$                                      | 2.8 ± 0.3          |
| $\text{C}_3\text{H}_6$                                      | 1.4 ± 1.0          |
| <i>i</i> - $\text{C}_4\text{H}_{10}$                        | 1.7 ± 1.0          |
| <i>n</i> - $\text{C}_4\text{H}_{10}$                        | 5.5 ± 5.3          |
| <i>i</i> - $\text{C}_5\text{H}_{12}$                        | 3.1 ± 2.8          |
| <i>n</i> - $\text{C}_5\text{H}_{12}$                        | 1.6 ± 1.4          |
| <i>n</i> - $\text{C}_6\text{H}_{14}$                        | 0.8 ± 0.2          |
| <i>n</i> - $\text{C}_7\text{H}_{16}$                        | 0.5 ± 0.2          |
| <i>n</i> - $\text{C}_8\text{H}_{18}$                        | 0.28 ± 0.09        |
| <i>n</i> - $\text{C}_{10}\text{H}_{22}$                     | 0.15 ± 0.06        |
| <i>n</i> - $\text{C}_{16}\text{H}_{34}$                     | 0.23 ± 0.05        |
| $\text{C}_6\text{H}_6$                                      | 1.1 ± 0.3          |
| $\text{C}_6\text{H}_5\text{-CH}_3$                          | 2.5 ± 0.9          |
| <i>p</i> + <i>m</i> - $\text{C}_6\text{H}_4(\text{CH}_3)_2$ | 0.52 ± 0.11        |
| <i>o</i> - $\text{C}_6\text{H}_4(\text{CH}_3)_2$            | 0.12 ± 0.04        |
| $\text{C}_6\text{H}_5\text{-C}_2\text{H}_5$                 | 0.53 ± 0.17        |
| CO  | 960 ± 350          |

mixing ratios are rather low, especially the alkyl aromatics are present only at some 10 ppt levels. Again we can see that the relative decrease between polluted and remote areas is more pronounced for the more reactive species, that is the pattern of the trace gas mixing ratio changes systematically as we go from polluted areas to remote locations: the abundance of a given hydrocarbon compound decreases the more rapidly the more reactive the compound is.

There is another point which deserves interest, the more reactive hydrocarbons such as propene or xylene show considerably higher mixing ratios in October than in May-June, whereas the more stable species such as  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$  or CO or even  $\text{C}_6\text{H}_6$  remain essentially unchanged. This is just what would be expected if photochemical

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TABLE III  
Average hydrocarbon mixing ratios from three series of measurements at a remote continental site in West Germany (Deuselbach).

| Compound  | Volume mixing ratios (ppb) |               |             |              |
|---|----------------------------|---------------|-------------|--------------|
|   | 18-20 May 1983             | 3-7 June 1983 | 22-23       | October 1983 |
| CH <sub>4</sub>   | 1740 ± 23                  | 1740 ± 37     | 1740 ± 10   |              |
| C <sub>2</sub> H <sub>6</sub>   | 2.33 ± 0.38                | 1.98 ± 0.18   | 1.84 ± 0.22 |              |
| C <sub>3</sub> H <sub>8</sub>   | 0.45 ± 0.14                | 0.47 ± 0.32   | 0.71 ± 0.40 |              |
| C <sub>3</sub> H <sub>2</sub>   | 0.55 ± 0.18                | 0.52 ± 0.13   | 0.64 ± 0.20 |              |
| C <sub>3</sub> H <sub>6</sub>   | 0.54 ± 0.10                | 0.40 ± 0.13   | 0.86 ± 0.12 |              |
| C <sub>4</sub> H <sub>6</sub>   | 0.08 ± 0.03                | 0.07 ± 0.03   | 0.33 ± 0.24 |              |
| <i>i</i> -C <sub>4</sub> H <sub>10</sub>  | 0.20 ± 0.07                | 0.17 ± 0.11   | 0.28 ± 0.10 |              |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub>  | 0.40 ± 0.15                | 0.39 ± 0.29   | 0.71 ± 0.28 |              |
| <i>i</i> -C <sub>5</sub> H <sub>12</sub>  | 0.27 ± 0.15                | 0.31 ± 0.20   | 0.37 ± 0.22 |              |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub>  | 0.12 ± 0.05                | 0.16 ± 0.13   | 0.22 ± 0.08 |              |
| <i>n</i> -C <sub>6</sub> H <sub>14</sub>  | 0.05 ± 0.02                | 0.08 ± 0.07   | 0.10 ± 0.05 |              |
| C <sub>6</sub> H <sub>6</sub>   | 0.10 ± 0.04                | 0.15 ± 0.07   | 0.12 ± 0.04 |              |
| C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub>                                      | 0.11 ± 0.06                | 0.18 ± 0.12   | 0.22 ± 0.09 |              |
| <i>p</i> + <i>m</i> -C <sub>6</sub> H <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> | 0.02 ± 0.01                | 0.03 ± 0.02   | 0.06 ± 0.03 |              |
| <i>o</i> -C <sub>6</sub> H <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub>            | 0.02 ± 0.01                | 0.02 ± 0.01   | 0.04 ± 0.01 |              |
| C <sub>6</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5</sub>                        | 0.04 ± 0.02                | 0.06 ± 0.05   | 0.07 ± 0.04 |              |
| CO  | 240 ± 28                   | 227 ± 27      | 213 ± 25    |              |

oxidation is responsible for the above mentioned difference in the relative abundance of the hydrocarbons between the urban and the remote continental atmosphere: the average OH radical concentration in the atmosphere at midnorthern latitudes is in autumn considerably lower than in summer,<sup>6</sup> thus all effects due to reactions with OH radicals such as the photochemical removal of hydrocarbons are bound to be substantially less pronounced in October than in May-June. However, a much broader data base will be necessary to substantiate this assumption. Other processes—especially transport—cannot yet be ruled out as possible explanations for these observations.

Measurements from a completely different continental area are shown in Table IV. Five air samples were collected in the Arabian Desert in Upper Egypt on 7 and 8 August 1982. In order to

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TABLE IV  
Hydrocarbon mixing ratios in desert areas in Upper Egypt (average and variance from five samples collected on 7 and 8 August 1982).

| Compound   | Mixing ratio (ppb) |
|--|--------------------|
| CH <sub>4</sub>  | 1733 ± 30          |
| C <sub>2</sub> H <sub>6</sub>  | 2.38 ± 0.42        |
| C <sub>3</sub> H <sub>8</sub>  | 0.22 ± 0.07        |
| C <sub>3</sub> H <sub>2</sub>  | 0.30 ± 0.06        |
| C <sub>3</sub> H <sub>6</sub>  | 0.45 ± 0.13        |
| C <sub>4</sub> H <sub>6</sub>  | 0.11 ± 0.02        |
| <i>i</i> -C <sub>4</sub> H <sub>10</sub>                                 | 0.11 ± 0.02        |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub>                                 | 0.27 ± 0.11        |
| <i>i</i> -C <sub>5</sub> H <sub>12</sub>                                 | 0.09 ± 0.03        |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub>                                 | 0.09 ± 0.02        |
| C <sub>6</sub> H <sub>6</sub>  | 0.19 ± 0.04        |
| C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub>                           | 0.22 ± 0.08        |
| <i>o</i> -C <sub>6</sub> H <sub>4</sub> ·(CH <sub>3</sub> ) <sub>2</sub> | 0.03 ± 0.02        |
| C <sub>6</sub> H <sub>5</sub> ·C <sub>2</sub> H <sub>5</sub>             | 0.05 ± 0.03        |
| CO   | 248 ± 34           |

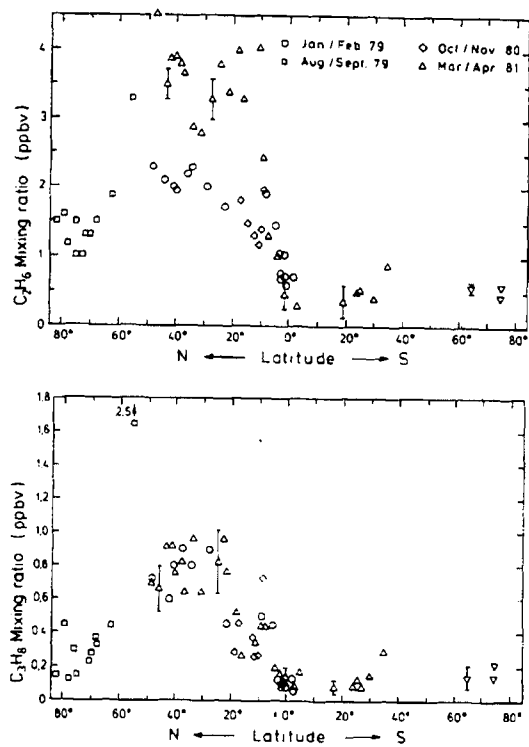
minimize systematic effects from local sources, the samples were taken at two different sites several ten kilometers apart. Although the mixing ratios of the different hydrocarbons are quite low and the trace gas pattern looks somewhat different from that observed at Deuselbach, it is evident that the sampled air masses were to some extent influenced by anthropogenic hydrocarbon sources. This is not particularly surprising since Egypt is a quite densely populated country but these results indicate that it is quite difficult to find continental areas at midnorthern latitudes which are really free from the impact of anthropogenic hydrocarbon emissions.

#### HYDROCARBONS IN THE MARINE ATMOSPHERE

During a number of cruises of RS *Meteor* in the Atlantic we made about 100 measurements of light hydrocarbons. Since the marine environment is much less subject to anthropogenic influences than

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most continental sites, it seems interesting to compare some of these results with the hydrocarbon mixing ratios we found at remote continental sites. In Figure 3 we have plotted the mixing ratios of four different light hydrocarbons as function of the geographic



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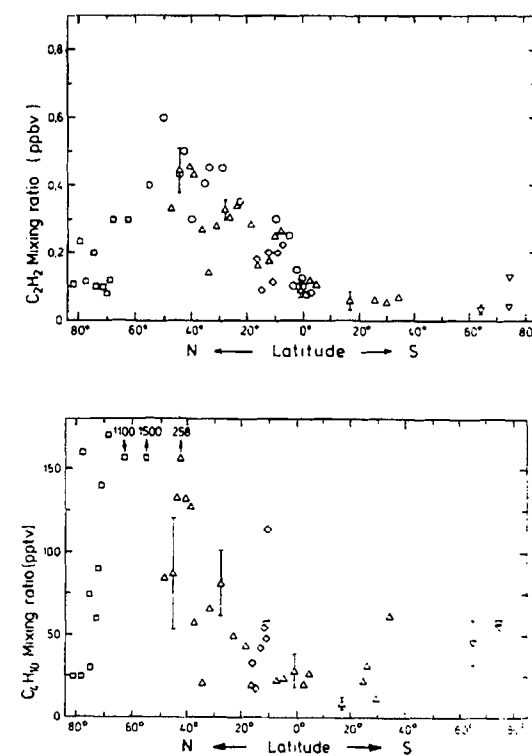


FIGURE 3 Mixing ratios of ethane, acetylene, propane and n-butane over the Atlantic as function of latitude. The data points with error bars represent the average and standard deviation of several data from less than 2 latitude range, collected within 24 h or less.

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latitude. If we compare these measurements with our data from remote continental sites, we can see that for  $C_2H_6$ ,  $C_3H_8$ , and  $C_2H_2$  the atmospheric mixing ratios over the Atlantic at midnorthern latitude are—within the observed scatter—similar to those found over the continents (Tables III and IV). However, *n*-butane (as well as *i*-butane and *n*- and *i*-pentane which are not shown here) is significantly less abundant in the marine atmosphere than over the continents. All four of the hydrocarbons shown in Figure 3 show a strong decrease in their mixing ratios between midnorthern latitudes and the equator and the southern hemispheric values are generally lower than the northern hemispheric mixing ratios. This can be explained by the existence of strong—most probably anthropogenic—sources for these hydrocarbons at midnorthern latitudes. A quite different behaviour is observed for propene (Figure 4). The latitudinal profile for propene shows no significant interhemispheric gradient.

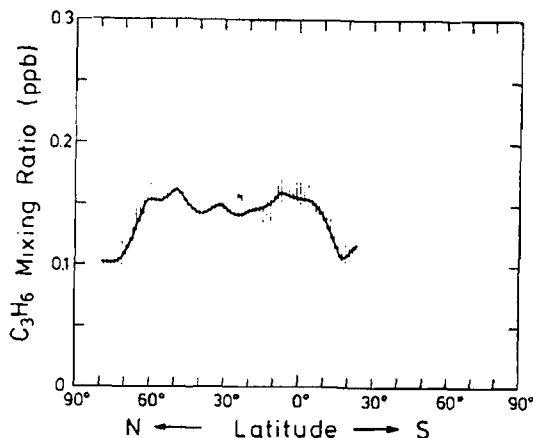


FIGURE 4 Running average of the propene mixing ratio over the Atlantic. The vertical bars indicate the error of the averaged propene mixing ratios.

#### HYDROCARBONS IN NON-URBAN ATMOSPHERE

With the exception of some more or less random variations, the propene mixing ratio is in the range of 0.12–0.18 ppb. These values are comparable to those we observed for remote continental areas. This is rather surprising if we consider that  $C_3H_6$  reacts much faster with OH radicals than  $C_2H_6$ ,  $C_2H_2$ ,  $C_3H_8$  or *n*- $C_4H_{10}$  (see Table I) and consequently will be more rapidly oxidized in the atmosphere. The most reasonable explanation for this is the existence of significant oceanic sources for propene. Indeed, it has been shown that propene and ethene are emitted from the oceans at rates which are sufficient to maintain the observed mixing ratios in the marine atmosphere.<sup>4</sup>

#### VERTICAL DISTRIBUTIONS OF SOME LIGHT HYDROCARBONS

The measurements we presented so far were all made on the ground and consequently (with one exception) within the planetary boundary layer. In this chapter some examples for vertical profiles of hydrocarbons up to altitudes well above the atmospheric boundary layer are shown. In autumn 1979 we made three flights with a Do-28 airplane and collected about 25 air samples in an altitude range between 300 m and 5.5 km. Some of the vertical profiles are shown in Figure 5. These flights were made over central Germany at 6°30' E–8° E/51° N–52° N on 30 October and 7 November. During all three flights a strong temperature inversion was observed at about 1.5 km altitude. Thus it is not surprising that a steep decrease of the trace gas mixing ratios with increasing altitude can be observed in the range from 1.5–2 km. Ethane and carbon monoxide decrease by a factor of 2,  $C_2H_2$  by a factor of 3, and  $C_2H_4$ , the most reactive of the four species, by a factor of 10. The mixing ratios below 1.5 km altitude are comparable to those from remote sites in Germany (see Table III), above 2 km the trace gas mixing ratios are extremely low. The existence of a pronounced inversion layer thus seems to influence the shapes of the vertical profiles considerably. Indeed, if we compare these data with the results of a flight made in March 1981 over the same area we can see significant differences. During this flight in March 1981 there was no temperature inversion and consequently the trace gas gradients were much less pronounced (see



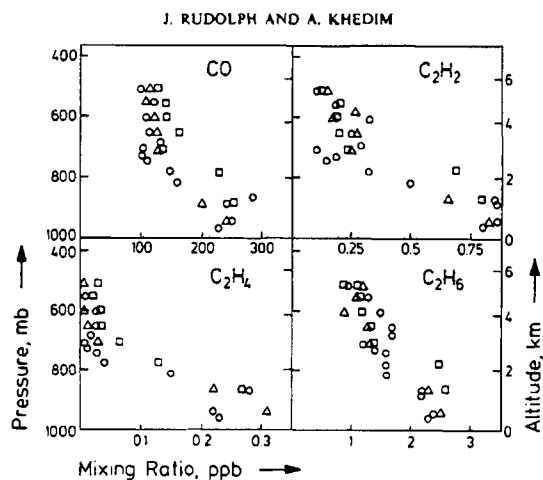


FIGURE 5 Vertical profiles of CO and C<sub>2</sub>-hydrocarbons over central Germany.

Triangles: 8° E, 52° N, 10:30-79, 16:00-16:30  
 Squares: 6° 30' E, 51° N, 10:30-79, 16:50-17:40  
 Circles: 6° 30' E, 51° N, 11:7-79, 12:10-13:00

Figure 6). CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> show only a very weak decrease in mixing ratios with increasing altitude. Only for C<sub>2</sub>H<sub>6</sub> we can observe some considerably elevated mixing ratios at lower altitudes.

### CONCLUSIONS

Light and medium molecular weight hydrocarbons are present in the remote troposphere at low but not negligible mixing ratios. Due to their relatively high reaction rate constants with OH radicals in the atmosphere the non-methane hydrocarbons may significantly affect the photochemistry of the remote atmosphere.

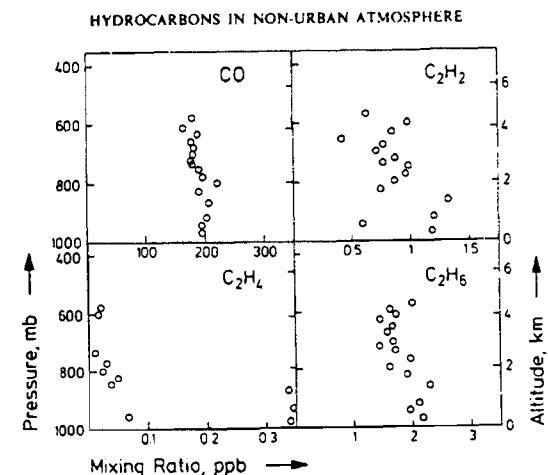


FIGURE 6 Vertical profiles of CO and C<sub>2</sub>-hydrocarbons measured over Germany on 22 March 1981, 14:30-15:30.

For a given area the atmospheric mixing ratios of the various hydrocarbons depend strongly on horizontal and vertical transport. Even in quite remote places the hydrocarbons show a considerable variability. In general the more reactive species show a faster decrease with decreasing influence of anthropogenic sources than the less reactive hydrocarbons such as C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>2</sub> or C<sub>3</sub>H<sub>4</sub>. The latter have more or less well defined background mixing ratios with a considerable systematic latitudinal dependence. However, these more stable compounds only have a limited importance for the atmospheric chemistry over remote areas. For these areas reactive species with local sources can be considerably more important, e.g. ethene and propene over the oceans.

The presented picture of the distribution of non-methane hydrocarbons is far from being complete. Neither cover our data for all kinds of remote locations nor is the list of hydrocarbons complete.

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Nevertheless, the presented data prove that the non-methane hydrocarbons are an important part of the chemistry of the atmosphere not only in polluted areas but also in the non-urban troposphere.

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### References

1. U. Schmidt, A. Khedim, F. J. Johna, J. Rudolph and D. H. Ehhalt. Preprint volume: *Second Symposium on the Composition of the Nonurban Troposphere*, May 25-28, 1982, Williamsburg, VA (American Meteorological Society, Boston, MA), pp. 52-55.
2. R. A. Duce, V. A. Mohnen, P. R. Zimmerman, D. Grosjean, W. Cantreels, R. Chatfield, R. Jaenicke, J. A. Ogven, E. D. Pellissari and G. T. Wallace, *Rev. Geophys. Space Phys.* **21**, 921 (1983).
3. R. F. Hampson and D. Garvin (eds.), *Reaction Rate and Photochemical Data for Atmospheric Chemistry*, National Bureau of Standards Special Publication 513 (U.S. Government Printing Office, Washington, D.C., 1977).
4. J. Rudolph and D. H. Ehhalt, *J. Geophys. Res.* **86**, 11959 (1981).
5. K. Sexton and H. Westberg, *Atmospheric Environ.* **18**, 1125 (1984).
6. A. Volz, D. H. Ehhalt, R. G. Derwent and A. Khedim, *Messung von atmosphärischem  $^{14}\text{CO}$ : eine Methode zur Bestimmung der troposphärischen OH-Radikalkonzentration*. Berichte der Kernforschungsanlage Jülich. Jül 1604, Jülich 1979, pp. 58-59.